



(19) Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

0 613 925 A1

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 94300982.9

(51) Int. Cl. 5: C08L 25/14, C08F 279/02,  
//C08L25/14,25:04,51:04)

(22) Date of filing: 10.02.94

(30) Priority: 03.03.93 US 25606

(71) Applicant: NOVACOR CHEMICALS  
(INTERNATIONAL) S.A.

(43) Date of publication of application:  
07.09.94 Bulletin 94/36

Fribourg, Canton of Fribourg (CH)

(86) Designated Contracting States:  
AT BE CH DE DK ES FR GB GR IE IT LI LU MC  
NL PT SE

(72) Inventor: Colella, Michael  
221 West Main Street  
Plantsville, CT, 06479 (US)  
Inventor: Marcoulier, Brian  
372 Theresa Street  
Fitchburg, MA, 01420 (US)

(74) Representative: Jukes, Herbert Lewis et al  
Swann, Elt & Company  
31 Beaumont Street  
Oxford OX1 2NP (GB)

(54) Highly transparent tough polymer blends.

(57) There is a demand for very clear tough polymers or polymer blends, particularly in the packaging industry. Crystal polystyrene is clear but lacks toughness. HIPS is tough but lacks the required clarity. Blends of styrene-ester polymers with a very small amount of HIPS do provide a very clear tough polymer alloy.

925 A1

The present invention relates to clear, toughened blends having a low haze. These blends are useful in household articles and rigid packaging such as containers or e.g. boxes.

General purpose or crystal polystyrene is used in a number of applications, including household and rigid packaging, where clarity or translucency is required. While general purpose polystyrene is suitable for such applications, it has a fairly low toughness. That is, it has low impact resistance. This drawback can be overcome by incorporating rubber into the polystyrene but it results in a loss of clarity or increasing haze.

United States Patent 5,079,296, issued January 7, 1992 to the assignee herein, discloses clear tough alloys. However, to obtain the combination of clarity and toughness, it is necessary to use a three component system, namely:

- 10 (i) a brittle polymer which is a clear thermoplastic;
- (ii) a block copolymer (typically K resin ®); and
- (iii) an impact modified polymer (e.g. HIPS).

The K resin ® is a relatively expensive component in the above blend. Applicants have discovered a blend having high clarity and good toughness while eliminating an essential component of the 296 patent.

15 There is a need for a relatively tough, clear polymer blend.

The present invention provides a polymer blend comprising:

- (i) from 95 to 99.5, preferably from 99 to 97, weight % of a copolymer comprising:
  - (a) from 70 to 90 weight % of one or more C<sub>8-12</sub> vinyl aromatic monomers which are unsubstituted or substituted by a C<sub>1-4</sub> alkyl radical; and
  - (b) from 30 to 10 weight % of one or more monomers selected from : C<sub>1-4</sub> alkyl esters of C<sub>3-6</sub> ethylenically unsaturated carboxylic acids; and
- (ii) from 5 to 0.5, preferably from 3 to 1, weight % of an impact modified polymer comprising:
  - (a) from 4 to 15 weight % of a rubbery polymer selected from from:
    - (i) co- and homopolymers of one or more C<sub>4-6</sub> conjugated diolefins; and
    - (ii) copolymers comprising:
      - (A) from 60 to 80 weight % of one or more C<sub>4-6</sub> conjugated diolefins; and
      - (B) from 40 to 20 weight % of one or more C<sub>8-12</sub> vinyl aromatic monomers which are unsubstituted or substituted by a C<sub>1-4</sub> alkyl radical,

25 to which has been grafted at least a portion of:

- (b) from 85 to 96 weight % of a polymer prepared by polymerizing a monomer mixture comprising:
  - (i) from 100 to 70 weight % of one or more C<sub>8-12</sub> vinyl aromatic monomers which are unsubstituted or substituted by a C<sub>1-4</sub> alkyl radical; and
  - (ii) from 0 to 30 weight % of one or more C<sub>1-4</sub> alkyl esters of a C<sub>3-6</sub> ethylenically unsaturated carboxylic acid.

30 The present invention also provides a rigid container having a haze of less than 15%, preferably less than 10%, most preferably less than 8%, made from the compositions of the present invention.

Figure 1 is a plot of the haze as a function of the methyl methacrylate content in an alloy of a copolymer of styrene and methyl methacrylate containing 1.6% of high impact polystyrene.

In accordance with the present invention the first component in the blend is a styrene ester polymer.

35 The polymer is present in an amount from 95 to 99.5, preferably from 97 to 99 weight %.

Some polymers comprise:

- (a) from 70 to 90, preferably from 75 to 80, weight % of one or more C<sub>8-12</sub> vinyl aromatic monomers which are unsubstituted or substituted by a C<sub>1-4</sub> alkyl radical; and
- (b) from 30 to 10, preferably from 25 to 20, weight % of one or more C<sub>1-4</sub> alkyl esters of C<sub>3-6</sub> ethylenically unsaturated carboxylic acids.

45 Vinyl aromatic monomers for use in component (i) are e.g. styrene, alpha-methyl styrene, t-butyl styrene, and p-methyl styrene. Styrene is a particularly preferred monomer for use in the polymers of component (i) of the present invention.

In component (i) C<sub>1-4</sub> alkyl esters of C<sub>3-6</sub> ethylenically unsaturated carboxylic acids acid are e.g. 50 acrylate monomers such as methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate and butyl acrylate. Particularly preferred monomers are the methacrylate monomers e.g. methyl methacrylate and ethyl methacrylate.

In accordance with the present invention, the styrene ester polymer may be blended with a small amount of an impact or rubber modified polymer. The impact or rubber modified polymer may be a co- or 55 homo- polymer of polybutadiene onto which has been grafted at least a portion of a homopolymer or copolymer of one or more vinyl aromatic monomer(s) or a styrenic ester copolymer.

The rubber in the impact or rubber modified polymer may be a homo- or co- polymer of one or more C<sub>4-6</sub> conjugated diolefins, preferably butadiene. If the rubbery polymer is a homopolymer, it may have a

steric configuration. Some impact modified polymers incorporate high cis polybutadiene. That is, polybutadiene having not less than about 95, preferably greater than 98% of the polymer in the cis configuration. Such polymers are commercially available from the Polysar Rubber Corporation under the trade mark TAKTENE. Some impact modified polymers incorporate medium cis polybutadiene. That is,

- 5 polymers having from about 50 to 60, preferably 55 weight % of the polymer in the cis configuration. Such rubbers are commercially available from the Polysar Rubber Corporation and Firestone under the trade marks TAKTENE and DIENE, respectively.

The rubber in the impact or rubber modified polymer may be a copolymer comprising from 60 to 80 weight % of one or more C<sub>4</sub>-<sub>6</sub> conjugated diolefins and from 40 to 20 weight % of one or more C<sub>8</sub>-<sub>12</sub> vinyl aromatic monomers which are unsubstituted or substituted by a C<sub>1</sub>-<sub>4</sub> alkyl radical. Such rubbers are known as SBR rubbers and are commercially available from a number of sources.

Conjugated diolefin(s) are e.g. butadiene. Some vinyl aromatic monomers have been listed above.

The rubbery polymer may form from 4 to 15, most preferably from 4 to 10 weight % of the impact or rubber modified polymer. The rubber may be dispersed through a continuous matrix of clear rigid thermoplastic. Such polymers may be prepared by "dissolving" the rubber in the monomers which are polymerized to form the plastic. During the initial stages of polymerization, the rubber may form the continuous phase and the monomer/thermoplastic polymer form the discontinuous phase. Early in the polymerization, the system may invert and the rubber form the discontinuous phase and the monomer/thermoplastic phase form the continuous phase. When the system undergoes phase inversion, the dispersed rubber phase is not homogeneous. That is, usually the rubber phase has occluded monomer and thermoplastic resin within it (e.g. the rubber forms a boundary layer encompassing monomer and thermoplastic). In any event, some of the monomer is grafted to the rubber. Of course, not all the thermoplastic is grafted to the rubber but only a portion of it. For example, under free radical initiation (the best condition for grafting), about half of the rubber is grafted. Thus graft levels may be less than 5, e.g. from about 1 to 3 % of the thermoplastic.

The continuous resin phase or matrix of the impact or rubber modified polymer may form from 96 to 85, preferably from 94 to 90 weight % of the impact or rubber modified polymer. The resin phase or matrix may be a polymer prepared by polymerizing a monomer mixture comprising:

- 30 (i) from 100 to 70 weight % of one or more C<sub>8</sub>-<sub>12</sub> vinyl aromatic monomers which are unsubstituted or substituted by a C<sub>1</sub>-<sub>4</sub> alkyl radical; and  
(ii) from 0 to 30 weight % of one or more C<sub>1</sub>-<sub>4</sub> alkyl esters of a C<sub>3</sub>-<sub>6</sub> ethylenically unsaturated carboxylic acid.

If the resin which forms the continuous or matrix phase of the impact or rubber modified polymer is a homopolymer, it is preferably a homopolymer of styrene, alpha-methyl styrene, p-methyl styrene, or t-butyl styrene; most preferably styrene. The resulting polymer would most preferably be high impact polystyrene (HIPS) or homologues of HIPS based on the other preferred monomers.

If the resin which forms the continuous or matrix phase of the impact or rubber modified polymer is a copolymer, the preferred vinyl aromatic monomers are styrene, alpha-methyl styrene, p-methyl styrene, or t-butyl styrene, most preferably styrene; and the preferred ester monomers are methyl methacrylate and ethyl methacrylate.

In preparing the polymer blends of the present invention, adequate mixing of the components can be achieved by mechanical mixing in a suitable intensive mixer, preferably an extruder. Operation of an extruder to achieve this end is within the purview of a person skilled in the art. For example, for an inch and a half extruder having an L to D ratio of about 24:1, the extruder is operated at from 30 to 150, preferably from 50 to 135, most preferably from 75 to 100, RPM. During such operation, the barrel temperature of the extruder is in the range of from 190° to 240° C, preferably from 200° to 220° C.

The components of the blends of the present invention may be dry blended in, for example, a tumble blender. The resulting blend may then be extruded. In an alternative procedure, the polymers may be fed directly to an extruder which provides good mixing.

50 Embodiments of the invention will be illustrated with reference to the following examples which should not be construed so as to limit the scope of the present invention. In the examples, unless otherwise specified, part(s) by weight (g), and per cent is weight %. Fig.1 mentioned below is by example.

## MATERIALS

55

In the examples, the following materials were used. Crystal polystyrene (Crystal) was one of the comparative materials. It is a homopolymer of styrene. Two types of impact polystyrene containing two different levels of polybutadiene, about 8% and 4%, high impact polystyrene (HIPS) and medium impact

polystyrene (MIPS)), were used. The copolymers used were copolymers of styrene and methyl methacrylate. The styrene content in the copolymers was about 90%, 80%, 70%, and 45% (Copolymer I, II, III, and IV, respectively).

The blends were prepared by dry blending the components and then passing them through laboratory 5 extruders to prepare pellets.

#### TEST METHODS

The pellets of the blends and pellets of comparative materials were molded into test specimens and 10 rigid containers. The haze of the samples was determined on injection molded plaques 1/8 of an inch (.3175 cm) thick using ASTM D-1003 (values in per cent), and the Gardner type impact strength was measured on injection molded rigid containers with a wall thickness of 0.060 inches (values in inch-pounds) (1.524 cm values in J). The impact test was conducted with a 5/8 inch (1.587 cm) tup and a 1/4 pound (.1134 kg) weight.

15

#### RESULTS

The compositions and the test results are set forth in Table 1 and Figure 1.

20

TABLE 1

COMPOSITION	HAZE (%)	IMPACT STRENGTH (IN. LBS.) (J)
CRYSTAL POLYSTYRENE	1.0	0.9 (0.01)
COPOLYMER II	0.5	1.4 (0.015)
CRYSTAL + 1.6% HIPS	40.4	-
COPOLYMER I + 1.6% HIPS	11.2	-
COPOLYMER II + 1.6% HIPS	5.4	3.1 (0.035)
COPOLYMER II + 3.0% MIPS	5.1	-
COPOLYMER III + 1.6% HIPS	12.2	-
COPOLYMER IV + 1.6% HIPS	43.3	-

25

30

35

Table I clearly shows that the compositions of the present invention provide a low haze product which is toughened relative to crystal polystyrene and significantly clearer than crystal polystyrene modified with small amounts of HIPS. Figure 1 is a plot of the haze as a function of the methyl methacrylate content in an 40 alloy of a copolymer of styrene and methyl methacrylate containing 1.6% of high impact polystyrene. Figure 1 may be used to determine the useful range of copolymer composition for obtaining adequate clarity.

45

It will be appreciated that the present invention is relevant to the demand for very clear tough polymers or polymer blends, particularly in the packaging industry. Crystal polystyrene is clear but lacks toughness. HIPS is tough but lacks the required clarity. Blends of styrene-ester polymers with a very small amount of HIPS do provide a very clear tough polymer alloy.

In the present application, any numerical value includes the precise value and any value "about" or "substantially" the same as the precise value. The wording of the appended claims and abstract is hereby incorporated into the present description.

50

#### Claims

1. A polymer blend characterised by comprising or consisting essentially of:

(1) from 97 to 99 weight % of a copolymer comprising or consisting essentially of:

(a) from 70 to 90 weight % of one or more monomers selected from : styrene, alpha-methyl styrene, p-methyl styrene, and t-butyl styrene; and  
 (b) from 30 to 10 weight % of one or monomers selected from : methyl methacrylate, ethyl methacrylate, methyl acrylate, and butyl acrylate; and

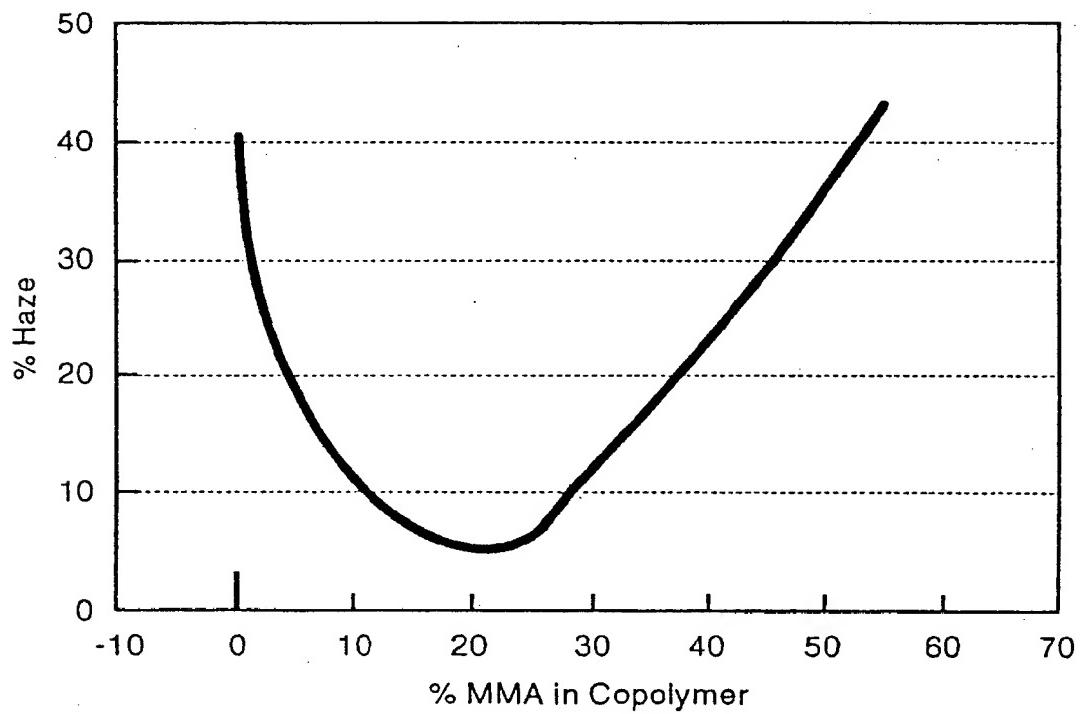
- (2) from 3 to 1 weight % of an impact modified polymer comprising or consisting essentially of:
- (a) from 4 to 15 weight % of a rubbery polymer selected from:
    - (i) co- and homo-polymers of C<sub>4</sub>-6 conjugated diolefins; and
    - (ii) copolymers comprising:
      - (A) from 60 to 80 weight % of one or more C<sub>4</sub>-6 conjugated diolefins; and
      - (B) from 40 to 20 weight % of one or more monomers selected from : styrene, alpha-methyl styrene, p-methyl styrene, and t-butyl styrene,
- to which has been grafted at least a portion of:
- (b) from 85 to 96 weight % of a polymer prepared by polymerizing a monomer mixture comprising:
    - (i) from 100 to 70 weight % one or more monomers selected from : styrene, alpha-methyl styrene, p-methyl styrene, and t-butyl styrene; and
    - (ii) from 0 to 30 weight % of one or more monomers selected from : methyl methacrylate, ethyl methacrylate, methyl acrylate, and butyl acrylate.
2. The polymer blend according to claim 1, characterised by that wherein component 1 comprises or consists essentially of:
- (a) from 75 to 80 weight % of one or more monomers selected from : styrene, alpha-methyl styrene, p-methyl styrene, and t-butyl styrene; and
  - (b) from 25 to 20 weight % of one or more monomers selected from : methyl methacrylate, ethyl methacrylate, methyl acrylate, and butyl acrylate.
3. The polymer blend according to claim 2, characterised by that wherein component 2 is an impact modified polymer comprising or consisting essentially of:
- (a) from 4 to 15 weight % of polybutadiene, to which has been grafted at least a portion of;
  - (b) from 96 to 85 weight % of a polymer prepared by polymerizing styrene.
4. The polymer blend according to claim 3, characterised by that wherein component 2 is an impact modified polymer comprising or consisting essentially of:
- (a) from 4 to 10 weight % of polybutadiene, to which has been grafted at least a portion of;
  - (b) from 96 to 90 weight % of a polymer prepared by polymerizing styrene.
5. The polymer blend according to claim 4, characterised by that wherein component 1 comprises or consists essentially of:
- (a) from 75 to 80 weight % of styrene; and
  - (b) from 25 to 20 weight % of methyl methacrylate.
6. A method of preparing a polymer blend according to any one of claims 1 to 5, characterised by incorporating together the corresponding components defined in any one of those claims.
7. A rigid container, characterised by comprising a polymer blend according to any one of claims 1 to 5.
8. A rigid container according to claim 7, characterised by the rigid container having a haze of less than 15%.
9. Packaging, characterised by comprising a polymer blend according to any one of claims 1 to 5.
10. A household article, characterised by comprising a polymer blend according to any one of claims 1 to 5.

50

55

Figure 1

% HAZE vs. MMA In Copolymer  
with addition of 1.6% HIPS





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 0982

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	FR-A-2 348 234 (GULF OIL) * page 2, line 2 - line 30 * * claims 1-6,8; examples 1,3 * ---	1-5	C08L25/14 C08F279/02 //(C08L25/14, 25:04,51:04)
A	EP-A-0 208 382 (DOW) * column 3, line 51 - column 4, line 10 * * claims 1,6-8; examples 3-5 * ---	1,2	
A	US-A-3 868 434 (R.C.WESTPHAL ET AL.) * column 1, line 66 - column 2, line 6 * * claims 1-5; example 16 * -----	1,2,7,10	
TECHNICAL FIELDS SEARCHED (Int.Cl.5)			
C08L C08F			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	4 July 1994	Engel, S	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			